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Studies of Arsenic Mobilization with Iron, Manganese and Copper in Borehole Sediments of the River Padma

M. Sarifuzzaman[1], M. N. A. Siddique[1], Farhana Khanam Ferdousi[1], Etmina Ahmed[1], A.M. Shafiqul Alam[1*] and Shah Mohammad Ullah[2]

[1]*Department of Chemistry, University of Dhaka Dhaka-1000, Bangladesh.*

[2]*Department of Soil, Water and Environment, University of Dhaka Dhaka-1000, Bangladesh.*

Abstract

Previous research suggested that there is a strong interrelation between As, Fe and Mn in their occurring, transport and exposure to the environment. In this context, a comparative study was conducted in this current experiment to correlate As, Fe, Cu and Mn by determining their concentration in sediments (upper & bore hole) at different depths in the river Padma. Six locations were selected as sampling sites from entering point (upstream) and end point (downstream) of the river Padma. Sampling was carried out by borehole technique at several depths ranging from 1 meter to 5 meters. The samples were digested with $HClO_4$- HNO_3 acid mixture of ratio 2:3 in an acid digestion bomb. Arsenic was determined by HVG-AAS technique and Fe, Mn and Cu were determined by Flame-AAS technique. Large amount of Fe has been obtained, which has endorsed the previous assumptions of the relations of As with Fe. The small correlation value in case of As, Fe and Mn indicates that not all the minerals of arsenic and Mn but only hydroxides of Fe and Mn interfere with As. The small amount of Cu obtained indicated that any relation between sources and exposure of As and Cu and their interaction is yet to be found out.

Key word: *Arsenic, Sediments, Borehole sediment, Acid digestion, HVG-AAS, Correlation*

Introduction

Arsenic is harming the developing countries like India and Bangladesh more vehemently owing to obvious reason. The Bengal Delta Plain has become one of the most severely contaminated parts in the world [1]. It has been reported that arsenic comes from the Himalayas through the rivers. The Himalayas contain rock, one of whose ingredients are arsenic bearing different pyrites for thousands of years. The rivers such as the Ganges originating from the apexes of the Himalayas enters Bangladesh as the Padma river at Chaipai-Nawabgonj and the river water carries soils and sediments containing the minerals which then spreads or by leaching to the wide regions of neighboring districts [2,3,4]. Arsenic was first detected in tube well water at Chaipai –Nawabgonj in 1993 [5]. The researcher seemed that arsenic might be mobilized through the Padma River formed alarming situation of arsenic contamination at the neighboring districts of the river Padma. Since river could be changed her path due to breaking the bank and creating the new bank, so arsenic might be leached from upper riverbed to the lower for a several years. It is evident that arsenic is not found in tube well water from 150 km far away district (Naogaon). As a result, high amount of arsenic was found in neighboring and down stream districts of the river Padma.

Several NGOs only collected the tube well water and arsenic was analyzed by the kit method. However, there is no adequate information about the mobilization of arsenic through the Padma river water from entering (Godagari) and ending point (Chandpur). Arsenic has metalloid properties and was found at trace level in earth crust like other metals (Fe, Cu, Mn) and it

*Corresponding Author E-mail: *amsalam2004@yahoo.com*

cannot solvate in normal aqueous system. When iron is released from pyrite (FeS_2) and arsenopyrite (FeAsS) as a Fe^{2+} in river water then arsenic has a possibility for leaching from upper layer to bottom sediments or mobilized to the river water from upstream to down stream.

The diagenetically derived secondary amorphous iron, manganese, and copper hydroxides can adsorb arsenate. These arsenic-adsorbed solid phases are transported, entrapped and deposited at the sediment-water interface in the sediments [7, 8]. So it is a great concern of the environmental chemists to estimate some other metals (such as Fe, Cu, Mn, Pb, Cd, Zn, Cr, Hg, etc.) as well as Arsenic metal in the river sediments to the river Ganges (entered as the Padma in Bangladesh) to find out whether there is any relation exists between the source of contamination of metals and/or their interference.

The aim of this work is to see the mobilization of arsenic from upstream to downstream at different locations of the river Padma in Bangladesh of six locations like Godagari, Rajshahi, Iswardi, Manikgonj, Mowyaghat & Chandpur. The focal theme of this research is that the sediments with high arsenic content can play an important role in the ground water quality and consequently it also influences the concentration of the trace metals in both the water column and biota, if they are desorbed or become available to benthic organisms. Consequently after finding arsenic level in the sediment, the specific objective of the work is to evaluate the influence (Fe, Mn, and Cu) with arsenic on sediments.

Sampling locations

Six locations were selected as sampling sites at entering point (upstream) and end point (downstream) of the river Padma in Bangladesh. Sampling locations are: Godagari, Rajshahi, Iswardi, Manikgonj, Mouyaghat and Chandpur. Godagari is the entering point of the river Padma of Chapai-Nawabgonj district from the Murshidabad district of West Bengal in India. About 80 km faraway from Godagari, the second sampling was carried out in Padma near Rajshahi city. Third sampling was done in near Hardinge Bridge at Iswardi Thana of Padma district. It is about 110 km from the Rajshahi city. The fourth sampling was carried out at the Padma - Jamuna at Aricha-Goyalandaghat of Manikgonj district which is 120 km down stream location from the Iswardi. Mowyaghat at Munshigonj district was another borehole sampling location. It is 60 km down from the Aricha-Goyalanda Ghat. The last sampling was carried out in Padma-Meghna confluence at Chandpur district where the Padma is flown to the Bay of Bengal as the Meghna River.

All the sediment samples were collected at several depths ranging from 1 to 5 meters using1.5 inches (diameter) pipe through normal digging procedure. These were taken in plastic bottles and sealed with tapes and then taken to the laboratory for further analysis.

Digestion of soil and foodstuff

The sediment samples were digested according to the HNO_3 and $HClO_4$ (Analytical Grade) digestion method [9] by using a Teflon acid digestion bomb with metal jacket at 200^{o}C for two hours.

Chemical analysis

Arsenic was analyzed using the Hydride Vapor Generator (HVG-1, Shimadzu, Japan) attached with Atomic Absorption Spectrophotometer (AAS-680, Shimadzu, Japan.). The total arsenic content was determined from the generated arsine gas (AsH_3). Fe, Mn & Cu were analyzed using flame Atomic Absorption spectrophotometer (AAS-680, Shimadzu, Japan.) Using air-acetylene flame. All reagents and chemicals were of analytical grade. Preparation of reagents was made with de-ionized water. The analytical methods were checked analyzing SRM (Standard reference materials No 404F9229 KANTO CHEMICAL INC. Cho-ku, Tokyo Japan). The certified values were varied from 2 to 5%. The interferences of the matrix in the digested sediments were also checked with the addition of standard addition method. Very little interferences were observed (3-5.5%) during the analysis.

Results and discussion

Arsenic concentration was found to be varied from upper and down stream (Std. = ± 0.03~3.50, n=3) at different depths of every sampling location (shown in Table 1 and Table 2) due to geochemical, biogeochemical transformation and geophysical aspect of sediments, rocks and different ores present in soil. It was observed that most of the cases arsenic content increases with the increase of the depth. Previous research reports that arsenic content of sediment of the Jamuna – Padma – Meghna rivers system varies from 1.0-6.5 mg/kg depending on particle size of the sediment [10]. The average arsenic concentration in the

Table 1. **Arsenic with other metals concentration in borehole sediments on the river Padma at upstream, Godagari**

	Sampling site	As mg/kg	Fe g/kg	Cu mg/kg	Mn g/kg	Depth m	As mg/kg	Fe g/kg	Mn g/kg	Cu mg/kg
Upstream	Upper soil	14.41	31.54	32.51	0.64	1	44.98	24.54	0.43	92.51
	Edge sediment	19.81	24.96	37.48	0.21	2	35.57	22.51	0.19	102.49
						3	16.23	22.25	0.14	87.48
						4	32.45	24.63	0.26	90.01
						5	21.02	23.63	0.19	107.51

n=3, Sd. = ± 0.03~3.50

Table 2. **Arsenic with other metals concentration in borehole sediments on the river Padma at down stream, Mowyaghat**

	Sampling site	As mg/kg	Fe g/kg	Cu mg/kg	Mn g/kg	Depth m	As mg/kg	Fe g/kg	Mn g/kg	Cu mg/kg
Down stream	Upper soil	15.91	27.84	51.2	0.71	1	65.02	30.01	0.65	22.7
	Edge sediment	12.03	12.06	20.2	1.46	2	87.07	30.466	0.50	22.2
						3	92.82	21.24	0.44	37.0
						4	106.92	29.24	0.46	39.2
						5	444.02	30.18	0.90	47.2

upper stream borehole sediments (at 1-5 m depth) in different locations is shown in the Figure 1. The highest arsenic content was found in Mouyaghat (84.65 mg Kg^{-1}) at 5m depth, because this region has been receiving arsenic from the next upstream Padma-Jamuna confluence. On the other hand, low amount of arsenic was found in Manikgonj (2.57 mg Kg^{-1}) region. This may be due to the strong current which might swift arsenic from the Padma-Jamuna confluence.

Arsenic concentration at the downstream region is comparatively higher. Moreover, the results indicate that the arsenic concentration was higher in the deeper depth of sediment. This may be due to the leaching of arsenic during the lean period of the season. Among the Upper soil, edge sediment and Borehole sediments, arsenic content was found to be highest in the Borehole sediment. It is due to arsenic might be stagnant on upper soil whereas arsenic might be mobilized from the edge sediments by the river current which might hindrance the deposition of arsenic in the edge sediments rather than the stagnant upper soil. The average arsenic content in upper soil of up stream at different locations were varied from 1.51 mg Kg^{-1} to 23.09 mg Kg^{-1} whereas it ranged from 0.34 mg Kg^{-1} to 20.12 mg Kg^{-1} at down stream. In case of edge sediments the value of arsenic in upstream were varied from 0.51mg Kg^{-1} to 19.81mg Kg^{-1} whereas it ranged from 0.11 mg Kg^{-1} to 22.17 mg Kg^{-1} at down stream.

It is notable that among these three metals, Cu content was the lowest in the sediments indicating no significant relationship were between the sources of arsenic and Cu. At upper stream the average value of Fe, Mn and Cu were found to be 61585.00mg Kg^{-1}, 134.00mg Kg^{-1} and 33.60mg Kg^{-1} (at 1-5 m depth) in all the six locations respectively. On the other hand, at the down stream borehole sediments (at 1-5 m depth), the average values of Fe, Mn and Cu were 27770.0mg/Kg^{-1}, 474.00mg/Kg^{-1} and 18.97mg/Kg^{-1} respectively.

Higher Fe/As ratio and relatively lower Mn/As ratio were found in the borehole sediment. This is because the presence of more soluble Fe-oxides and hydroxides rather than insoluble Fe-silicate in the borehole sediments of the river Padma. However, lower Cu/As ratio is found in borehole sediments of different depth. This may be due to the transportation of Cu from the water stream to sediments, being rapidly re-mobilized from the solids and Cu is then transferred back to the water stream.

However, in spite of high content of Fe along with arsenic, the small correlation coefficient value (such as r=0.384) indicates that not all the Fe forms are associated with the transport and release mechanism. Some of the forms such as oxy-hydroxides are associated. On the other hand, the linear regression analysis shows that arsenic is weakly correlated with manganese (Mn) content in sediment samples. These relationships suggest that arsenic might be related to Mn at some depths, whereas, in several other stations, they were inversely related. Previous researchers established that iron ores are always enriched with arsenic whereas no arsenic was found in manganese ores [7]. Finally, the relation between arsenic and Mn obtained concludes that there may be some relationship between arsenic and Mn such as adsorption and co-precipitation of As with Mn Figure 2.

Very small amount of Cu in every samples indicates that there is no relation between the sources of arsenic and Cu. Again, very small correlation co-efficient indicates the absence of any relation during occurrence, transport and release between them.

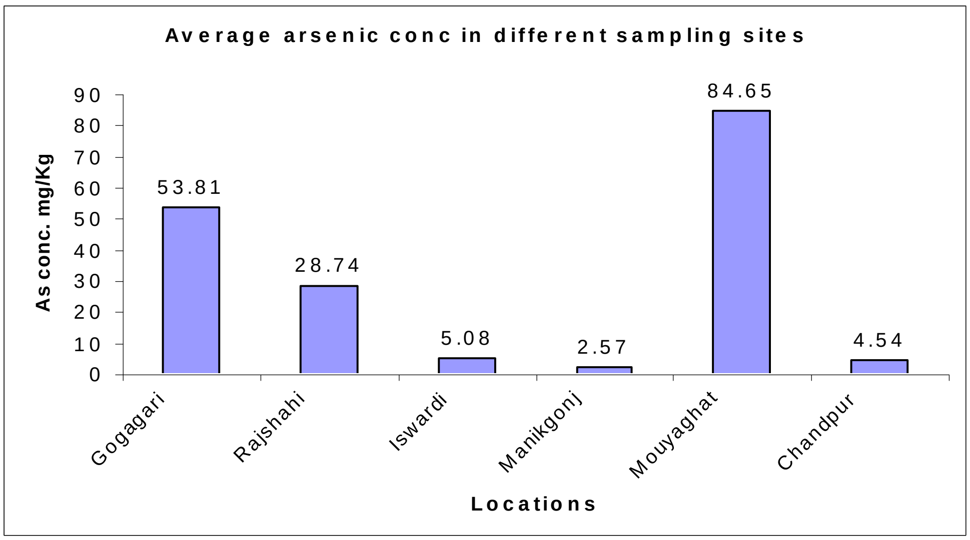

Figure 1. **Average arsenic conc in different sampling sites**

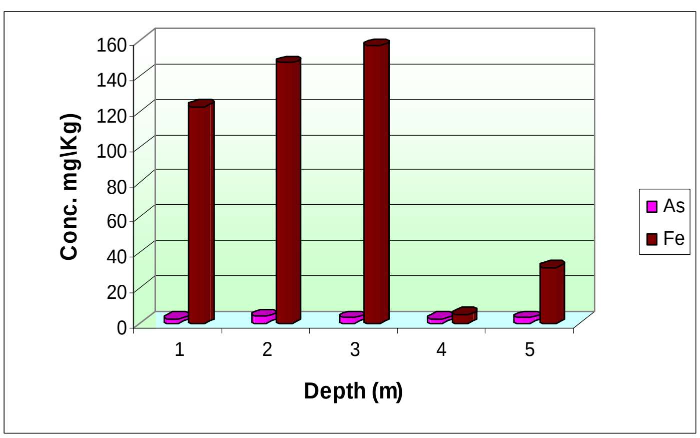

Figure 2. **Correlation of As with Mn at upstream of Godagari, Chapai-Nawabgong (Correlation Co-efficient r=0.4361)**

Conclusion

It can be concluded that arsenic was mobilized from one location to another and as a result the variation in arsenic content was found in different locations. Finally it might be deposited to the lower sediments. It is evident that arsenic was already found in tube well water of Rajshahi, Iswardi, Manikgonj, Moyaghat near Faridpur and also near downstream location of the river Padma at Chandpur. The study also suggests that the distribution of arsenic in the sediments is not only controlled by single mineral phase, but arsenic may be partitioned into three phases: metal (Fe and Mn) hydroxides, Fe sulfides, and also organic matter. Arsenic is slightly correlated to Fe and it is more lower correlated with Mn and Cu. It has also been observed that the river Padma changes its course of path in every rainy season or during the flood; as a result, deposited arsenic from the fresh land of the Padma River might be leached to the shallow aquifers, which in turn shows higher content of arsenic in water of the new tube wells installed at neighboring locations of the river Padma.

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A. M. Shafiqul Alam joined in the department of Chemistry at Dhaka University, Bangladesh in 1978. Since then Prof. Alam is working in the field of Analytical & Environmental Chemistry.